

Oxygen and Iron Production by Electrolytic Smelting of Lunar Soil 14641

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Previous work has shown that Fe^0 and O_2 can be derived by electrolysis from silicate melt of a composition typical of lunar soils (Lindstrom and Haskin 1979). In the present study, our goal is to refine further the conditions necessary to optimize production and to determine efficiencies of production (how much product is derived for a given current) and purity of products. These depend on several factors, including potential imposed between electrodes, configuration and surface area of the electrodes, composition of the electrolyzed silicate melt, and oxygen fugacity. We have designed experiments to measure the dependence on these variables of three parameters that must be known before production by electrolysis can be optimized. These parameters are:

Limiting Current = $f[\text{anode surface area (ASA), cathode surface area (CSA), distance between electrodes (d), electrolyte composition (X), potential between electrodes (E)}$

Actual Current = $f[\text{ASA, CSA, X, E, reduction potentials of electroactive species (E}^0\text{), diffusion rates of electroactive species (D)}$

Efficiencies of Production = $f(X, E, f\text{O}_2)$.

The limiting current is the maximum current the electrolyte can sustain at a given potential. It is related to the intrinsic conductivity of the bulk electrolyte. The conductivity has been measured previously for several compositions (Lewis 1985), and the limiting current can be calculated from these values.

For a direct current to flow through the electrolyte, oxidation and reduction of electroactive species must take place at the anode and cathode. Therefore, the actual current depends on reduction potentials and concentrations of electroactive species in the melt, as well as the electrode surface areas, and in general will be somewhat less than the limiting current. Once this dependence is understood, the actual current can be optimized to the limiting current by adjusting ASA, CSA, and E. Because different reactions are occurring at the anode and cathode, the effect of ASA on the current is not necessarily the same as the effect of CSA. Therefore, it is necessary to measure their effects independently. We did this by using a three-electrode experimental set-up, one electrode to establish a reference potential and the other two as working electrodes. This permitted the total potential to be divided into the potential driving

the anodic reaction plus the potential driving the cathodic reaction. In this way, we have determined the dependence of current on ASA, CSA, E, and X.

We have developed a method for measuring O_2 yield and, therefore, O_2 production efficiency. The amount of O_2 produced is based on the difference in sample weight before and after the experiment. We have found a simple relationship which explains most of the variation in production efficiency for O_2 . Mainly, efficiency decreases in proportion to the competing oxidation of Fe^{2+} to Fe^{3+} .

Determination of efficiency of Fe production has proven more difficult because of the solubility of Fe^0 in the Pt wire loops used to hold the samples and the reduction of Si^{4+} . However, we have estimated Fe efficiencies indirectly from the differences in current at various potentials. Experiments were designed to determine the difference between "background" current flow (related to reductions other than Fe) and total current flow. These values were determined by measuring current flow as a function of potential for both a silicate melt containing Fe and a silicate melt in which a molar-equivalent amount of electro-inactive MgO had been substituted for FeO. We found that Fe efficiency increases regularly with increasing FeO concentration and decreases with increasing potential. The decrease in efficiency with increasing potential is related to the increasing amount of Si^{4+} that is reduced at higher potentials, suggesting that the purity of the Fe product also decreases with increasing potential.

In summary, we have determined the three relationships above for several compositions over a range of potentials from 0 to about 1 volt. With this information, the three equations can be solved simultaneously to optimize ASA, CSA, E, X, and fO_2 for optimum production rate or production efficiency. Furthermore, because these relationships are general, rather than specific to a preconceived electrolytic set-up, these data will be applicable to whatever electrolytic set-up further research finds to be most practical.

An abstract describing these results which was published in *Lunar and Planetary Science XX* follows.

Some Effects of Composition on Efficiencies for Production of O_2 and Fe^0 From Silicate Melts by Electrolysis, R. O. Colson and L. A. Haskin, Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, Missouri

Several experiments have been conducted aimed at determining the efficiencies for production of O_2 and Fe metal by electrolysis of silicate melts. Efficiency of O_2 production [defined as the moles of O_2 produced/(moles of electrons passed through the melt/4)] is calculated from the amount of O_2 produced and the measured total

current flow. The amount of O_2 produced is determined from the difference in sample weight before and after the experiment. Efficiency of Fe metal production was determined by a combination of theoretical treatment and experiment. Experiments were designed to determine the difference between "background" current flow (related to reductions other than Fe) and total current flow. These values were determined by measuring current flow as a function of potential for both a silicate melt containing Fe and a silicate melt in which a molar-equivalent amount of electro-inactive MgO has been substituted for FeO. Because the duration of these Fe-efficiency experiments is short and the species being reduced are not significantly depleted, these estimates correspond to the case in which the melt being electrolyzed is continuously "refreshed" and well stirred (except that oxidation products from the anode are not reduced at the cathode).

Efficiencies of production will be influenced by the presence of reducible or oxidizable species other than the species of interest. For example, O_2 production is expected to be made less efficient by the concurrent oxidations of $Fe^{2+} \rightarrow Fe^{3+}$ and $Fe^0 \rightarrow Fe^{2+}$ (we have found a significant amount of Fe^0 to be soluble in the silicate melt, similar to solubilities of Ni^0 , Co^0 , and Zn^0 found by Semkow et al.¹). Fe^0 production is expected to be made less efficient by reductions such as $Fe^{3+} \rightarrow Fe^{2+}$, $Si^{(4+)} \rightarrow Si^0$, $Cr^{3+} \rightarrow Cr^{2+}$, and $Ti^{4+} \rightarrow Ti^{3+}$; however, Cr and Ti are not present in the experiments of this study. We expect the efficiencies of O_2 or Fe production to decrease as the relative amounts of competing species increase and as electrode potentials approach the reduction potentials of the competing reactions. Therefore, it is useful to look at efficiencies as a function of (1) electrode potential, (2) oxygen fugacity, and (3) melt composition (in specific, Fe concentration).

O_2 Efficiency.— O_2 efficiencies as a function of electrode potential are shown in Figure 1.22. The low point in the oxygen efficiency curve is near the reduction potential for Fe^{3+} which, as expected, is the region of minimum efficiency. (Based on Fe^{3+} reduction potentials, we estimate about 35–65% of the Fe^{2+} is oxidized at these potentials.) At low potentials, a small amount of Fe^{2+} is oxidized to Fe^{3+} (we estimate 5–10%) and at higher potentials the amount of Fe^{2+} that is oxidized is small compared to the amount of oxygen because oxygen is much more abundant in the melt than Fe.

O_2 efficiency as a function of fO_2 at constant potential and constant total Fe concentration is shown in Figure 1.23. The efficiency is lower at lower fO_2 , consistent with the higher concentration of Fe^{2+} at the lower fO_2 and, therefore, a larger fraction of current is related to the oxidation of Fe^{2+} . For this change in oxygen fugacity, the fraction of current attributable to $Fe^{2+} \rightarrow Fe^{3+}$ increases by 65%, and calculations based on the report of Sack et al.² indicate an increase of 55% in Fe^{2+} concentration. If we

assume that all the current is related to oxidation of either oxygen ions or Fe^{2+} , we can choose the equation $\% \text{Fe}^{2+} / \% \text{O}_2 = X(\text{Fe}^{2+}) / X(\text{O}^{2-})$ to represent relative amounts of the current attributable to each oxidation, where $\% \text{Fe}^{2+}$ is the percentage of the current attributed to the oxidation of Fe^{2+} and $X(\text{O}^{2-})$ is the effective concentration of oxidizable oxygen (which we assume is constant for the series of compositions between diopsidic and hedenburgitic melts used in this study). The equation can be modified (assuming $\% \text{Fe}^{2+} + \% \text{O}_2 = 100\%$) to yield $\% \text{O}_2 / (100 - \% \text{O}_2) = X(\text{O}^{2-}) / X(\text{Fe}^{2+})$. This relationship predicts that as Fe^{2+} concentrations increase, O_2 efficiency will decrease. This is the relationship observed and shown in Figure 1.24.

Fe Efficiency.—Figure 1.25 plots cathodic current as a function of electrode potential for several compositions. The "background" current is for a composition in which MgO has been substituted for FeO . This current is related primarily to the reduction of Si^{4+} . If we assume that no current is lost to electronic conduction,³ then the figure gives a rough estimate of the relative amounts of the total current that can be attributed to the Fe^{2+} and Si^{4+} reductions at various potentials and Fe concentrations. However, for these compositions and potentials, most, if not all, of the reduced Fe is dissolved in the melt or Pt electrodes and does not exist as (readily extracted) pure metallic Fe . Threshold potentials for the precipitation of pure metallic Fe can be calculated from the data presented in Grove.⁴ Threshold potentials so calculated are plotted as a function of Fe concentration in Figure 1.26. Comparison of Figures 1.25 and 1.26 indicates that in the range of potentials we have studied, pure metallic Fe can only be precipitated at concentrations of $\text{Fe} > 35$ mole% FeO and, at those concentrations, the amount of Fe reduced will be very large compared to the amount of Si^{4+} reduced. These results indicate that high efficiencies of O_2 and Fe production can be achieved by electrolysis, but not in bulk melt of the same composition. High efficiencies of O_2 production are favored by low Fe concentrations, and high Fe^0 production efficiencies are favored by high Fe concentrations.

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References

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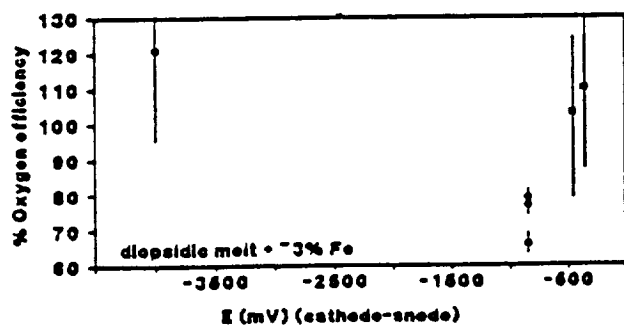


Figure 1.22

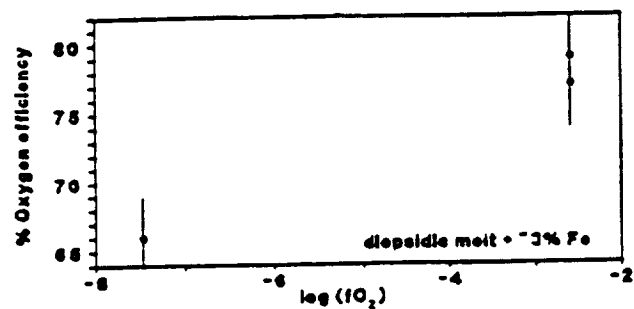


Figure 1.23

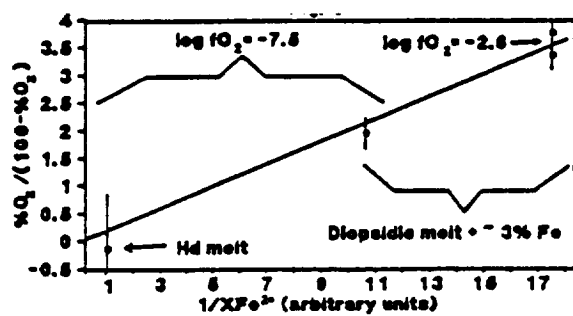


Figure 1.24

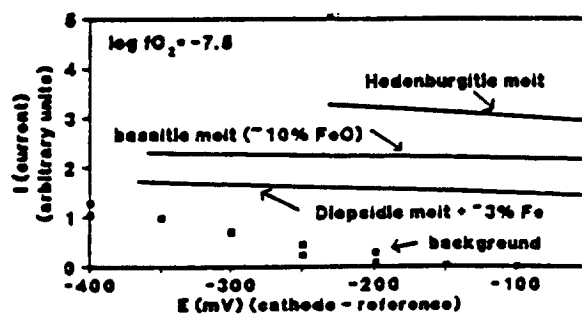


Figure 1.25

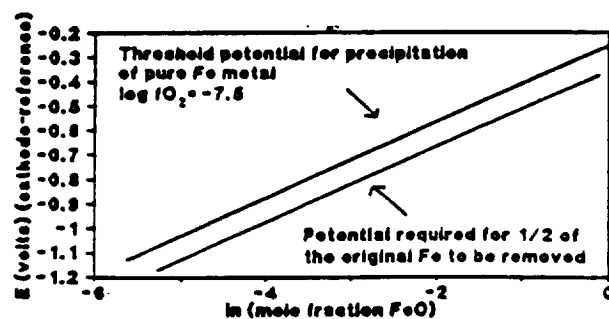


Figure 1.26

II. MATERIAL PROPERTIES